165/11-8-74
MLM-2184

22-104/
MLM-2184

**Mound Laboratory Isotopic
Power Fuels Programs:
July-September 1974**

October 25, 1974

AEC Research and Development Report

Monsanto

MOUND LABORATORY

Miamisburg, Ohio
operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company
for the

U. S. ATOMIC ENERGY COMMISSION

U. S. Government Contract No. AT-33-1-GEN-53

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FOREWORD

This report presents the technological achievements of Mound Laboratory in its isotopic fuels programs during the past three months. This work is supported by the AEC Division of Space Nuclear Systems.

Previous reports in this series are:

MLM-2014	MLM-2099
MLM-2122	MLM-2122
MLM-2166	MLM-2166

TABLE OF CONTENTS

	<u>Page</u>
SUBSTOICHIOMETRIC STUDIES	4
<p>Plutonium-238 dioxide particles were reduced to $^{238}\text{PuO}_{1.86}$ in vacuum at 1900°C. Microscopic examination revealed the characteristic two-phase structure of $^{238}\text{PuO}_{2-x}$ in the reduced particles. Upon oxidation, the two-phase structure was still observable, although thermogravimetric analysis shows that the particles were stoichiometric.</p>	
METHOD FOR PREPARING METAL CARBIDES	7
<p>Ignition of tricyanomethide salts provide a new method of preparing metal carbides. Unusual carbides, such as $\text{Cr}_{0.62}\text{C}_{0.35}\text{N}_{0.03}$, may be prepared by controlling the temperature of ignition of the tricyanomethide salt.</p>	

SUBSTOICHIOMETRIC STUDIES

The microstructural changes that occur during reduction, oxidation, and reheating of $^{238}\text{PuO}_2$ particles are being studied using MHW (Multihundred Watt) feed material.

These changes are being investigated by preparing particles of different stoichiometries and, subsequently, oxidizing them over a range of time and temperature to see what, if any, changes occur and under what conditions these changes take place.

Particles of $^{238}\text{PuO}_2$ of known stoichiometry were prepared by reducing the particles in vacuum for 30 min at 1900°C . The stoichiometry was determined from data obtained from thermogravimetric analysis, TGA, to be $^{238}\text{PuO}_{1.86}$. A portion of these reduced particles was oxidized on the TGA balance in air for 6 min at 800°C . A second portion was placed in a platinum tube furnace and oxidized by heating in air for 5 hr at 600°C .

The particles were prepared for microscopic examination and etched for 10 min in a 1:1 HCl-HF solution. The as-reduced substoichiometric particles (Figures 1 and 2) showed a two-phase structure (Figures 3 and 4). However, data obtained from TGA confirmed that the particles are stoichiometric.

The results of these initial experiments clearly indicate that the structural changes which take place on reduction are still observable after the particles are oxidized to their correct stoichiometry. There appears to be little difference between the particles that were oxidized by heating to 800°C for 6 min in air and the particles that were oxidized by heating in air at 600°C for 5 hr. Since it has been determined that the microstructures are retained after oxidation, efforts are being directed toward determining their stability limits with respect to further heat treatment. (C. B. Chadwell and W. D. Pardieck)

FIGURE 1 - Particles of $^{238}\text{PuO}_2$ before reduction. (250X)

FIGURE 2 - Reduced substoichiometric particle showing a two-phase structure. This structure is characteristic of substoichiometric $^{238}\text{PuO}_{2-x}$. (250X)

FIGURE 3 - Particle of PuO₂ after being oxidized in air on the TGA balance for 6 min at 800°C. The two-phase structure is retained after oxidation.

FIGURE 4 - Particles of PuO₂ after being oxidized in air for 5 hr at 600°C. Comparison of Figures 3 and 4 shows little change in microstructure, although oxidation time and temperature were different.

METHOD FOR PREPARING METAL CARBIDES

With the advent of commercial electric power generation by nuclear means, there arises a need for hard, corrosion resistant substances for purposes which include reactor construction materials and nuclear fuel forms. Since materials which are of such corrosion resistance and hardness to be suitable for the nuclear industry are likely to be required in large amounts, it would be very desirable to be able to produce such materials inexpensively, efficiently, and in various forms, sizes, and shapes. One substance which appears to have considerable promise as a material for the commercial nuclear industry is the carbides of various metals. The toughness of many metal carbides is well known. Herein is a novel method of preparing metal carbides which does not require gaseous hydrocarbons, the careful blending of metal oxide and carbon powders in the correct proportions, or the handling of finely divided and possibly flammable metal powders.

It has been known for many years that the tricyanomethide ion, $C(CN)_3^-$, commercially available as potassium tricyanomethide, forms many metal salts of low solubility. These salts are easily prepared in the laboratory by a simple metathesis reaction such as indicated schematically in Reaction 1 below

which precipitates the metal tricyanomethide salt. In Reaction 1, M^{2+} might be divalent chromium, Cr^{2+} , for example. That these salts, which can easily be prepared in good purity and homogeneity, might serve as starting materials for the preparation of metal carbides does not appear to have been suggested heretofore. A sample of a tricyanomethide salt, chromium(II) tricyanomethide, prepared as described elsewhere,¹ was placed in a vacuum furnace (10^{-4} mm Hg total pressure) and was ignited to 1200°C for 90 minutes. A black material resulted which appeared to be a mixture of a light, fluffy powder and a coarse, dense, granular material. The light, fluffy powder was separated from the dense material by blowing with a stream of air. The x-ray powder pattern of the dense material was then obtained and compared to the x-ray powder patterns of known chromium compounds. The powder pattern of the unknown material gave twenty-three identifiable lines, each corresponding exactly to the lines of the well-characterized carbide of chromium Cr_3C_2 . This established that chromium carbide Cr_3C_2 is a product of the decomposition by heat in vacuum of chromium(II) tricyanomethide. The exact mechanism of the decomposition reaction was not investigated, but for present purposes (to show that Cr_3C_2 is a reasonable product of the decomposition of $Cr[C(CN)_3]_2$) it may be represented by Reaction 2.

The temperature of the decomposition reaction may be controlled to give new and otherwise difficult to prepare carbides. For example, when chromium(II) tricyanomethide was heated in vacuum at 600°C, a dark material was obtained which gave an x-ray powder pattern containing five identifiable lines which exactly matched those of the known² chromium carbon nitride $Cr_{0.62}C_{0.35}N_{0.03}$.

As another example of this technique, a sample of ferrous tricyanomethide, $Fe[C(CN)_3]_2$, was prepared. When ignited in vacuum at 1200°C for 90

minutes, a black residue was obtained. This residue gave an x-ray powder pattern consisting of 10 identifiable lines. Five of these lines corresponded to the known pattern of the carbide FeC and five to the pattern of metallic iron. The presence of metallic iron may indicate decomposition of some of the iron carbide between the temperatures 25°C and 1200°C. Other iron carbides, such as cementite, Fe₃C, are known to have temperature regions between 25°C and 1200°C where they are unstable with respect to decomposition to the elements. (G. L. Silver)

REFERENCES

1. G. L. Silver, Inorg. Nucl. Chem. Letters, 4, 533 (1968).
2. P. Ettmayer, Monatsh. Chem., 97, 1248 (1966).